Degradation Kinetics of Xylose and Glucose in Hydrolysate Containing Dilute Sulfuric Acid

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Abstract: In preparation of fuel alcohol from biomass as feedstock, hydrolysis with dilute acid as catalyst is one way to produce fermentable saccharide, xylose and glucose. However, the acid is also the catalyst in degradation of xylose and glucose and the yield of sacchride is dependent on the kinetic behaviors of saccharide. The degradation kinetics of xylose and glucose in the hydrolysate was investigated under the conventional process conditions of hydrogen ion concentration from 0.05 to 0.2 mol/L and temperature from 150 to 200℃. With a numerical calculation method, the kinetic parameters were estimated, and the activation energy of xylose and glucose in the degradation reaction was obtained. The kinetic equations correlating the effect of hydrogen ion concentration on the rate constants of degradation reaction were established. Comparison between the calculated results from the equations and experimental ones proved that the established kinetic model could satisfactorily predict the degradation behavior of xylose and glucose in the acidic hydrolysate.

Key words: biomass; dilute sulfuric acid; xylose; glucose; kinetic behavior

CLC No.: TK6　　　**Document Code:** A　　　**Article ID:** 1009−606X(2008)06−1132−06

1　INTRODUCTION

Campbell et al.[1] used several different techniques to estimate the currently known crude oil reserves and the reserves as yet undiscovered and concluded that decline in the worldwide crude oil production would begin before 2010. As one of renewable energy sources, fuel alcohol produced from biomass has so far attracted research interest in development of various process technologies. So, there is no doubt that biomass containing lignocelluloses, such as sawdust, crop residues and grasses, will become one of the resources of renewable energy for needs of mankind[2]. If cellulose can be efficiently and economically converted into monosaccharide by hydrolytic processes, ethanol produced from biomass can make great contribution to future energy needs[3]. Xylose and glucose, the desired components formed in the hydrolysis, will be consecutively degraded to the undesired products which are the inhibitors in the next enzymatic hydrolysis and the later fermentation process[4], this degrading problem is a crucial one in the technological process of acidic hydrolysis[5−11]. The different degrading rates of xylose and glucose are the main factors affecting the overall yield of monosaccharide in the hydrolysis. Some researchers have studied the kinetic behaviors of pure xylose and glucose solution in a glass reactor[12], but it can not indicate the real behaviors of them precisely. In

this work the degrading behaviors were studied by using hydrolysate in a stainless steel reactor. The study of kinetic behaviors of xylose and glucose in the dilute acidic hydrolysate is the preliminary step to determine the technological parameters.

The general acceptance of acidic hydrolysis of lignocelluloses as the first order consecutive reaction does not concern with the different degrading rates of xylose and glucose or the influence of acid concentration on the degrading rates[13−15]. In this work, separate kinetic behaviors were observed and separate kinetic expressions were formulated so that a better understanding of degrading characteristics of monosaccharide in hydrolysate could be realized.

2　EXPERIMENTAL

2.1　Materials and Analysis Method for Hydrolysate

Hydrolysate from the runs of hydrolysis reactions of biomass of sawdust in dilute sulphuric acid was collected as experimental material. Monosaccharides were analyzed through external standard method on HPLC (LC-20AT, Shimadzu, Japan) and the detector was Polymer Laboratories PL-ELS 2100 (move phase acetonitrile:water=23:77(φ), total flow rate at 0.8 mL/min, nebulization temperature 40℃, gasification temperature 70℃, column intersil-NH₂, 4.6 mm×250 mm, 5-Micron). The main components besides

monosaccharide were qualitatively analyzed by GC–MS (Perkin-Elmer, Clarus500GC/MS: positive ionization as ionization mode, IE 70 eV, scanning 33~500 *m/z*, ion source temperature 250 ℃, interface temperature 250 ℃) and quantitatively by GC [Agilent, 6820GC, FID detector, innowax 30 m×0.32 mm×0.25 μm, carrier gas N_2 (99.999%), inlet temperature 250 ℃, detection temperature 300 ℃]. The TIC spectrum of hydrolysate is shown in Fig.1.

Through analysis of the mass spectrum, there are four main components in the hydrolysate, acetic acid (A), furfural (B), levulic acid (C) and hydroxymethyl furfural (D). And the concentrations of various components are listed in Table 1.
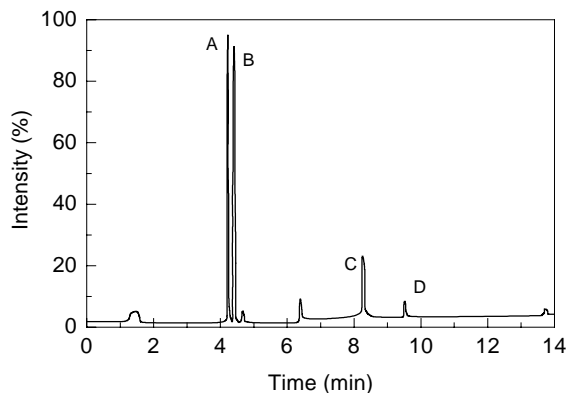

Fig.1 TIC spectrum of the hydrolysate

Table 1   Concentrations of main components in the hydrolysate

Component	Xylose	Glucose	Acetic acid	Furfural	Levulic acid	Hydroxymethyl furfural
Concentration (mg/mL)	27.51	35.49	0.786 0	0.397 0	0.261 0	0.035 00

2.2 Experimental Device

The reactor used is a stainless steel autoclave with 300 mL in capacity, which was produced by Tongchan High-pressure Container Co., Ltd. in Dalian, China. Other necessary components of the autoclave included sampling tube and magnetically driven stirrer which can eliminate the effect of mass transfer. The device is shown in Fig.2.
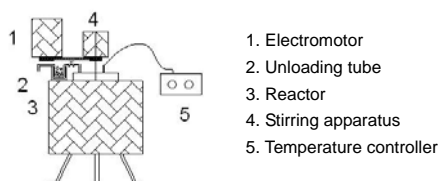

1. Electromotor
2. Unloading tube
3. Reactor
4. Stirring apparatus
5. Temperature controller

Fig.2 Schematic diagram of experimental device

3   EXPERIMENTAL RESULTS AND FORMULATION OF KINETIC EQUATIONS

The essential factors influencing thedegradation of monosaccharide in hydrolysate include catalyst concentration and reaction temperature. The concentration of hydrogen ion in the experiments varied from 0.05 to 0.2 mol/L, reaction temperature from 150 to 200 ℃. From analysis, many compounds were known to form in the reaction, and the products were complex.

3.1 Effect of Acid Concentration on Degradation of Monosaccharide

Sulfuric acid is the catalyst for degradation of monosaccharide in the hydrolysate. Experiments were carried out to investigate the effect of acid concentration on the degradation rate. Each run proceeded with various acid concentrations at the same temperature.

Figure 3 shows the experimental data obtained from 4 runs with the reaction temperatures of 150, 160, 170 and 180 ℃, indicating the variation of dimensionless concentration of xylose versus reaction time. The value of initial concentration c_{s0} was taken when the hydrolysate in the autoclave was heated to the desired reaction temperature. It is indicated in Fig.3 that at various reaction temperatures, the degradation rate of xylose increases with the hydrogen ion concentration and reaction temperature. So, the kinetic constant is the function of reaction temperature and hydrogen ion concentration.

And Fig.4 shows the degradation behavior of glucose at four reaction temperatures, i.e., 150, 160, 170 and 180 ℃. This figure indicates the variation of dimensionless concentration of glucose versus the reaction time. The value of initial concentration c_{s0} was taken when as the hydrolysate in the autoclave was heated to the desired reaction temperature. Fig.4 demonstrates the degradation behavior of glucose at four reaction temperatures with different hydrogen ion concentrations, indicating that at any one of the specific temperatures and the specific reaction times the degradation rate of glucose increases with the hydrogen ion concentration.

3.2 Comparison of Degradation of Monosaccharide in Hydrolysate

Monosaccharides in the hydrolysate here refer to xylose and glucose, the desired products from hydrolysis of biomass. The dependence of their degradation rates on the reaction temperature is different, as shown in Fig.5.

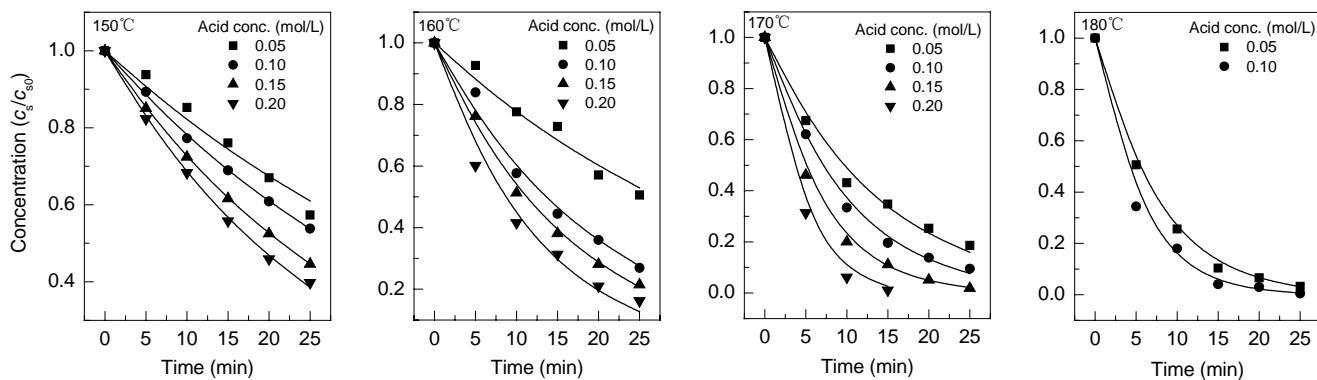The absolute value of degradation rate of xylose

Fig.3 Xylose concentration vs. time at various acid concentrations and temperatures
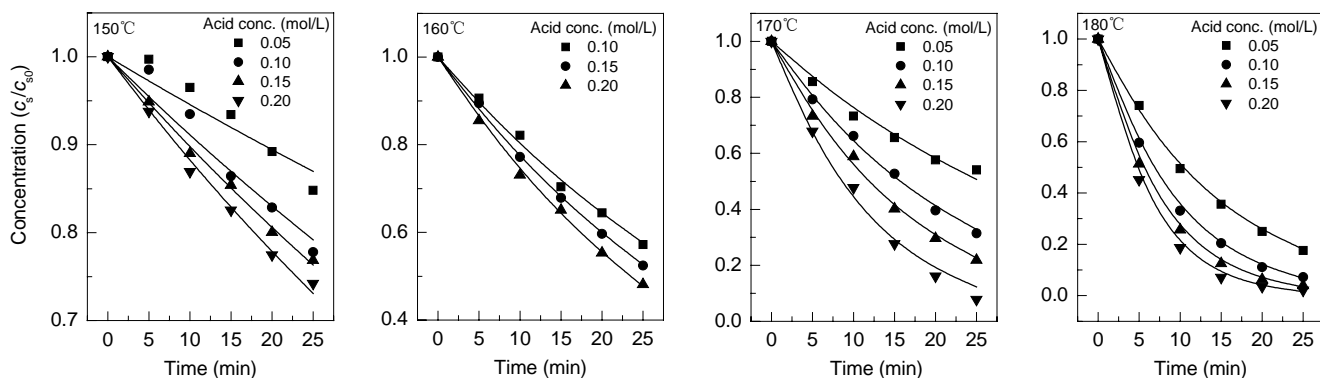

Fig.4 Glucose concentration vs. time at various acid concentrations and temperatures
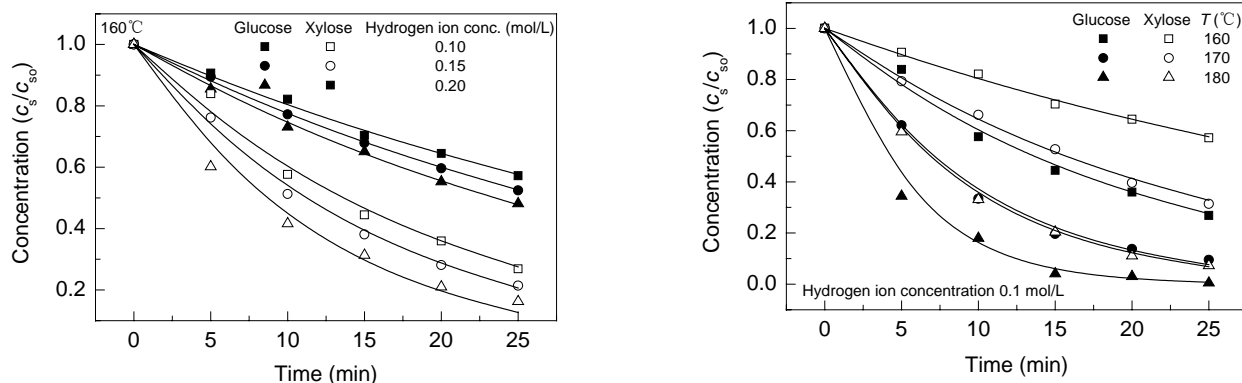

Fig.5 The relationship between monosaccharide concentration and reaction time at
different hydrogen ion concentrations and temperatures

increases more than that of glucose, but the relative percentage of degradation rate of glucose increases more than that of xylose with increasing of reacting temperature. This indicates that the degradation rate of glucose is more sensitive to the reaction temperature than that of xylose, and its activation energy is higher than that of xylose. And the other reason for this result is probably the effect of acidic medium. Because some of the ultimate products from the degradation of glucose are acidic compounds, such as formic acid and acetic acid, and these acidic compounds can inhibit the degradation. So these compounds can affect the

degradation rate constant to some extent.

3.3　Derivation of the Kinetic Model

In the acidic medium, the main products forming during the degradation reaction of monosaccharides detected by GC−MS are furfural and hydroxymethyl furfural (HMF). However, furfural and HMF account for only a portion of the monosaccharide loss observed during the degradation reaction. For the degradation of xylose at 190℃, at least 10 different products from the degradation besides furfural were identified, including formaldehyde, formic acid, crotonaldehyde, lactic acid, acetaldehyde, dihydroxyacetone, etc.[13]. Such results

are the same as those reported by Qian et al.[15]. On the other hand, glucose degraded to more complicated products than xylose did. In order to simplify the equation, all the degraded products were considered as lumped one, and the reaction can be expressed in terms of the following simple mode[16,17]:

$$S \xrightarrow{k} D, \tag{1}$$

and its rate equation can be thus expressed as follows:

$$-\frac{dc_s}{dt} = kc_s^n. \tag{2}$$

When the natural logarithms of xylose and glucose dimensionless concentrations from experiments were plotted against reaction time, a linear relationship was observed. So the degradation of xylose and glucose at constant reaction temperature and hydrogen ion concentration can be regarded as a first order reaction. The degrading behaviors of xylose and glucose at various reaction temperatures and acid concentrations were investigated and had the same results as those by former researcher using pure solution as feedstock[18].

Through integration under the assumption $n=1$, the following expression can be obtained from Eq.(2):

$$\ln\left(c_s/c_{s0}\right) = -kt. \tag{3}$$

As to the rate constant k, it contains the term of acid concentration $[H^+]$, because the degradation rate of either monosaccharide, as verified in the experiments, is affected by the acid concentration. With reference to the previous research of sawdust hydrolysis[17], the pre-exponential factor k_0' in Arrhenius equation, $k=k_0'\exp(-E/RT)$, can be expressed as:

$$k_0' = k_0[H^+]^a. \tag{4}$$

So, Eq.(4) can be rewritten in details as

$$k = k_0[H^+]^a \exp\left(-\frac{E}{RT}\right). \tag{5}$$

Consequently, the kinetic model for the first order degradation of monosaccharide can be expressed as:

$$-\frac{dc_s}{dt} = k_0[H^+]^a \exp\left(-\frac{E}{RT}\right)c_s, \tag{6}$$

or

$$\frac{c_s}{c_{s0}} = \exp\left[-k_0[H^+]^a \exp\left(-\frac{E}{RT}\right)t\right]. \tag{7}$$

4　PARAMETER ESTIMATION AND STATISTICAL TEST

4.1　Parameter Estimation

Equation (7) is an exponential expression which contains three parameters, k_0, pre-exponential factor, E,

activation energy, and a, order of the acid concentration. In order to determine the values of thes parameters, the method of least estimation is employed. Let

$$A = \sum_{i=1}^{M}\left[\left(c_s/c_{s0}\right)_{exp} - \left(c_s/c_{s0}\right)_{cal}\right]^2 \tag{8}$$

have the minimum value, and by using sets of experimental data, the values of the parameters are thus obtained. The values are listed in Table 2.

Table 2　The parameters of the kinetic equation of xylose and glucose degradation

Monosaccharide	E (kJ/mol)	a	k_0
Xylose	114.4	0.649	2.384×10^{11}
Glucose	136.8	0.673	4.834×10^{13}

4.2　Model Test

The results of statistical test are shown in Table 3, M is the times of experiment; M_p the number of parameters included in Eq.(7), and A the result of Eq.(8). And the calculating equations of decisive index R^2 and F-distribution are shown as the following Eqs.(9) and (10). The value of F at specific condition can be obtained for the table from statistical distributions[19].

Table 3　Results of the statistical test of models

Saccharide	Parameter					
	M	M_p	A	R^2	F	$10F_{0.05}$
Xylose	51	3	0.2423	0.9587	1648.58	27.900
Glucose	66	3	0.3017	0.9592	1834.62	27.459

$$R^2 = 1 - \sum_{j=1}^{M}\left[\left(c_s/c_{s0}\right)_{exp} - \left(c_s/c_{s0}\right)_{cal}\right]^2 \bigg/ \sum_{j=1}^{M}\left(c_s/c_{s0}\right)_{exp}^2, \tag{9}$$

$$F = \frac{\left[\sum_{j=1}^{M}\left(c_s/c_{s0}\right)_{exp}^2 - \sum_{j=1}^{M}\left[\left(c_s/c_{s0}\right)_{exp} - \left(c_s/c_{s0}\right)_{cal}\right]^2\right]\bigg/M}{\sum_{j=1}^{M}\left[\left(c_s/c_{s0}\right)_{exp} - \left(c_s/c_{s0}\right)_{cal}\right]^2 \bigg/\left(M - M_p\right)}. \tag{10}$$

Obviously, at the significance level of 5% and under the corresponding degree of freedom, the results indicate that the calculated value $F \gg 10F_{0.05}$, and $R^2 > 0.9$. Through calculation, the sum of mean residue square is 0.003319 for xylose model, and 0.00382 for glucose model. So the test indicates that the assumed kinetic models are feasible to describe the degradation behavior of monosaccharides in hydrolysate.

In order to show the accordance between experimental data and calculated ones directly, Fig.6 illustrates the calculated values against the experimental data of c_s/c_{s0}. The results of statistical test and the comparison of calculating data with experimental data show that the kinetic equations of xylose and glucose both are feasible and can describe the kinetic behavior accurately.

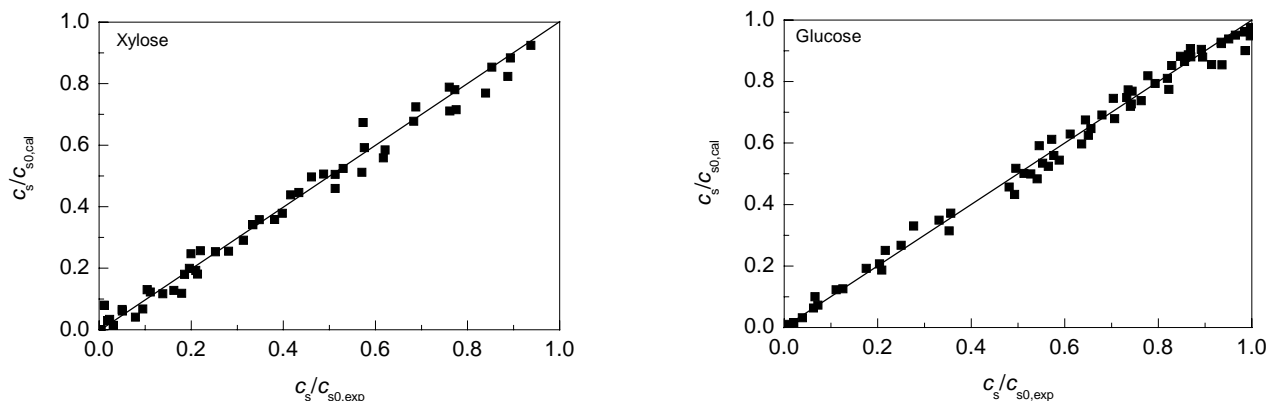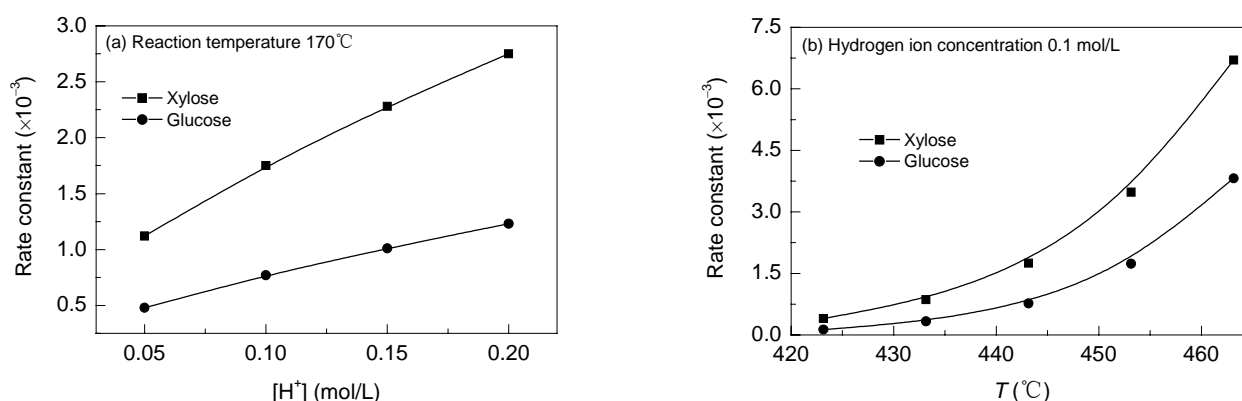So, the kinetics equation of degradation of xylose

Fig.6 Experimental data vs. calculated values of c_s/c_{s0}

Fig.7 Effects of hydrogen ion concentration and reaction temperature on the rate constant of xylose and glucose

is expressed as

$$-\frac{dc}{dt} = 2.384 \times 10^{11} [H^+]^{0.649} \exp\left(-\frac{114.4 \times 10^3}{RT}\right) c \ [\text{mol/(L·s)}], \quad (11)$$

and the kinetic equation of degradation of glucose is expressed as

$$-\frac{dc}{dt} = 4.834 \times 10^{13} \left[H^+\right]^{0.673} \exp\left(-\frac{136.8 \times 10^3}{RT}\right) c \ [\text{mol/(L·s)}]. \quad (12)$$

The kinetic equations of xylose and glucose indicate that the degradation activation energy values of xylose and glucose are 114.4 and 136.8 kJ/mol, which justify the assumption that the degradation activation energy of glucose is higher than that of xylose in the former part.

4.3 Comparison of Rate Constants between Xylose and Glucose

The rate constants of xylose and glucose at certain hydrogen ion concentration and reaction temperature can be obtained from the kinetic equations (11) and (12). So the effects of hydrogen ion concentration and reaction temperature on the rate constants are shown in Fig.7.

Figure 7 indicate that the dependence of both degradation rates on H^+ concentration and reaction temperature is different. Fig.7(a) shows that the degradation rate of xylose is more sensitive than that of glucose. As H^+ concentration varies from 0.05 to 0.2 mol/L, reaction rate constant of xylose increases more rapidly than that of glucose. However, the data shows that the ratio of the reaction rates increasing becomes less as H^+ concentration increases. The reason for this phenomenon is that there is no significant difference between reaction orders of H^+ in the degradation reaction of xylose and glucose.

Fig.7(b) shows that the reaction rate of glucose responds more sensitively to the variation of temperature than that of xylose. As reaction temperature varies from 150 to 160℃, for example, reaction rates increase by 112% and 145% for xylose and glucose respectively. It is because that the activation energy of glucose is higher than that of xylose, and the reaction rate of glucose more sensitive than that of xylose. Through comparison of the results in Fig.7, the reaction temperature has more influence on the degradation rates of both xylose and glucose than H^+ concentration does.

5 CONCLUSIONS

Degradation of monosaccharide, xylose or glucose with sulfuric acid as catalyst in biomass hydrolysate is a first order reaction, and its degradation rate is significantly affected by the hydrogen ion concentration in the hydrolysate. Based on the kinetic data of xylose and glucose degradation obtained from a stainless steel autoclave, a simplified kinetic model was developed taking all pathways into consideration. The best fit parameters were determined by nonlinear regression analysis. Comparisons of results calculated from the kinetic equations of xylose and glucose with the experimental ones proved that the kinetic model established in this work could satisfactorily predict the degradation of xylose and glucose over a broad range of acid concentrations. Degradation of xylose and glucose in the hydrolysate is a side by side reaction system, and the degradation reaction of xylose quicker than that of glucose. Careful selection of reaction conditions is necessary in order to obtain high yield of monosaccharide in acidic hydrolysis of biomass, because of differences in activation energy and degradation rate constant.

DENOTATION:

a	Order of acid concentration
A	Value of Eq.(8)
c_s	Saccharide concentration (g/L)
c_{s0}	Initial saccharide concentration at desired reaction temperature (g/L)
D	Products of saccharide degradation
E	Activation energy of saccharide degradation (J/mol)
F	Value of F-distribution
$[H^+]$	Hydrogen ion concentration (mol/L)
k	Rate constant
k_0	Constant
k_0'	Pre-exponential factor
M	Times of experiment
M_p	Number of parameters
n	Order of reactant concentration
R	Mole gas constant [J/(mol·K)]
R^2	Decisive index
S	Saccharide
t	Reaction time (s)

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